# PATENT ABSTRACTS OF JAPAN

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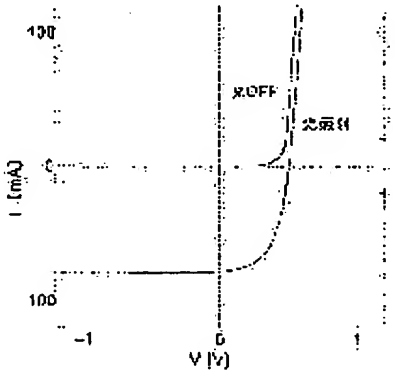
## (54) IRON SILICIDE SEMICONDUCTOR THIN FILM AND ITS MANUFACTURE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a manufacturing method, wherein photoelectric characteristic is controlled with respect to a β-FeSi2 or amorphous iron silicide semiconductor.
SOLUTION: The iron silicide semiconductor thin film is constituted, by changing optical band gap through hydrogenation. Alternatively, the same is constituted by controlling a carrier concentration through hydrogenation. Or the iron silicide semiconductor thin film is manufactured by a method, wherein hydrogen is mixed into a thin film, grown by the inflow of hydrogen gas into atmosphere upon forming the film to hydrogenate the β-FeSi2 or the amorphous FeSiX in the thin film growing method of the β-FeSi2 or the amorphous FeSiX.

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[Patent number]
[Date of registration]

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CLAIMS

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[Claim(s)]
[Claim 1]
The iron silicide semi-conductor thin film characterized by changing an optical band gap by hydrogenation.
[Claim 2]
The iron silicide semi-conductor thin film according to claim 1 characterized by consisting of beta-FeSi 2 of the range whose optical band gap is 0.6-1.1eV.
[Claim 3]
The iron silicide semi-conductor thin film according to claim 1 characterized by consisting of amorphous FeSiX (x being 1-infinity) of the range whose optical band gap is 0-1.85eV.
[Claim 4]
The iron silicide semi-conductor thin film characterized by controlling carrier concentration by hydrogenation.
[Claim 5]
The light and the electronic device characterized by using an iron silicide semi-conductor thin film according to claim 1 to 4.
[Claim 6]
The manufacture approach of claim 1 characterized by hydrogenating beta-FeSi 2 or amorphous FeSiX (x being 1-infinity) by mixing hydrogen into the thin film which flows and grows up hydrogen gas to be an ambient atmosphere at the time of membrane formation in the thin film grown method of beta-FeSi 2 or amorphous FeSiX thru/or an iron silicide semi-conductor thin film given in four.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to an iron silicide semi-conductor thin film and its manufacture approach.
[0002]
[Description of the Prior Art]
It is an ideal for a next-generation industrial ingredient not to have worries about a resource life, and to consist of only elements of a low environmental load mold. The atmospheric-air configuration element (N, O) which does not have the need of considering a resource life, as the candidate element, the very long element (Si, calcium, Ga) of a resource life, and an element with a high rate of recycling (Fe, Cu) can be considered.
[0003]
If the above idea is met, as an environmental ingredient, the various things of GaN, Cu2O, and beta-FeSi 2 grade can be considered with a semi-conductor, for example. Also in it, since beta-FeSi 2 is the semi-conductor of the direct transition mold in which an absorption coefficient has the large (it is -10-5cm-1 at visible wavelength) bunt gap of 0.85eV which can grow epitaxially on Si substrate, it attracts attention very much as a next-generation semiconductor material.
[0004]
As concrete application, optical device ingredients, such as an efficient solar-battery ingredient, a photodiode, and luminescence die ODOO, are mentioned, and patent application of the thing (JP,2001-64099,A) and solar battery (JP,11-103080,A) about the formation approach of beta-FeSi 2 thin film, and the things (JP,2000-133836,A, JP,2001-127338,A, JP,2002-57368,A, JP,2002-76431,A, the ** table No. 502477 [ 2001 to ] official report, etc.) about a light emitting device is carried out.
[0005]
[Problem(s) to be Solved by the Invention]
this invention persons developed the approach of depositing FeSi2 thin film of a parent phase previously, deposited on a substrate by the laser ablation method (JP,2000-178713,A). Furthermore, patent application was carried out about the approach of depositing FeSi2 thin film of the parent phase by the opposite target type DC sputtering method (application for patent 2001-386820). Moreover, also when a presentation ratio comes out almost as it is and changes into an amorphous condition very much recently, it reports that the film in which a semi-conductor property is shown is obtained ("collection of the 62nd Japan Society of Applied Physics academic lecture drafts" 1022 pages). This attracts attention similarly and patent application (an application for patent 2001-386824, application for patent 2001-387341) of the related invention is carried out September 11, 2001 and 1 on ("collection of Japan Society of Applied Physics Kyushu branch lecture meeting lecture drafts in Heisei 13 fiscal year" 86 page, and December 1, 2001).
The continuation film which formed membranes by such approach showed the 0.64-0.70eV optical band gap by the film of an amorphous condition, and beta-FeSi 2 film showed the 0.85-0.92eV optical band gap.
[0006]
While the light and the electrical property of beta-FeSi 2 are investigated by the detail recently, and is becoming clear and its light and electrical property are becoming whether to be ** gradually also about an amorphous iron silicide semi-conductor, those property control will be made into the big technical problem from now on. When using beta-FeSi 2 and an amorphous iron silicide semi-conductor to devices various from now on, control of

light and an electrical property is needed. Especially, reduction of carrier concentration, control, control of a band gap, etc. are indispensable.
[0007]
[Means for Solving the Problem]
this invention person found out that the above-mentioned technical problem was solvable with beta-FeSi 2 of an iron silicide semi-conductor, or hydrogenation of amorphous FeSiX (x is 1-infinity).
That is, this invention is an iron silicide semi-conductor thin film characterized by changing an optical band gap by hydrogenation.
Moreover, it is the above-mentioned iron silicide semi-conductor thin film characterized by this invention consisting of beta-FeSi 2 of the range whose optical band gap is 0.6-1.1eV.
Moreover, it is the above-mentioned iron silicide semi-conductor thin film characterized by this invention consisting of amorphous FeSiX (x being 1-infinity) of the range whose optical band gap is 0-1.85eV.
Moreover, this invention is an iron silicide semi-conductor thin film characterized by controlling carrier concentration by hydrogenation.
Moreover, this inventions are the light and an electronic device characterized by using the above-mentioned iron silicide semi-conductor thin film.
[0008]
Furthermore, this invention is the manufacture approach of the above-mentioned iron silicide semi-conductor thin film characterized by hydrogenating beta-FeSi 2 or amorphous FeSiX (x being 1-infinity) in the thin film grown method of beta-FeSi 2 or amorphous FeSiX by mixing hydrogen into the thin film which flows and grows up hydrogen gas to be an ambient atmosphere at the time of membrane formation.
[0009]
It sets to this invention and, for hydrogenation, hydrogen is mixing beta-FeSi 2 or amorphous FeSiX in a thin film at the time of thin film growth. It says combining with Si atom and/or Fe atom. hydrogenation -- amorphous FeSiX -- Fe -- it is the range of 0-1.85eV from the abbreviation zero in the case of being rich to 1.85eV of Si100% of case, and beta-FeSi 2 can change a band gap in 0.6-1.1eV. Therefore, hybridization of a light emitting and receiving elemnt and the wavelength of light which carries out **** can be optimized by adjustment of a band gap.
[0010]
Moreover, electric resistance, i.e., carrier concentration, is controllable by hydrogenating beta-FeSi 2 or amorphous FeSiX. Carrier concentration control is indispensable to the device design of a light emitting and receiving elemnt, a circuit, etc. Control of carrier concentration enables application to the electron device of this ingredient. Once the specific resistance which shows carrier concentration increases, it decreases, while the degree of hydrogenation becomes large. It is thought that it will have contributed to the generation of carriers if the hydrogen contained in beta-FeSi 2 or amorphous FeSiX is little, it carries out termination of the non-bonding electron which consists of Fe, Si, and H and is contained in the crystal rank of the crystal structure of a prismatic crystal, brings about reduction of carrier concentration and has the above included to some extent.
[0011]
[Embodiment of the Invention]
The iron silicide semi-conductor thin film of this invention can be manufactured using physical vapor growth, such as the usual thin film grown method, for example, the laser ablation method, the sputtering method, vacuum deposition, and the ion plating method, or a chemical-vapor-deposition method. By the difference in the substrate temperature bordering on 400 degrees C, hydrogenation beta-FeSi 2 film or hydrogenation amorphous FeSiX can be grown up.
[0012]
In the laser ablation method, it is flowing hydrogen gas into the ambient atmosphere at the time of the film growth which used laser radiation or the laser radiation to Fe target in the case of heated Si substrate for the laser radiation, or Fe and Si target to a FeSiX target coincidence or by turns, and adjusting the pressure of hydrogen gas, and beta-FeSi 2 or amorphous FeSiX to which the hydrogen content was adjusted is produced.
[0013]
Moreover, in the sputtering method, hydrogen gas is flowed into the rare gas for sputtering at the time of the film [ target / sputtering of a FeSiX target, or / Fe and Si target ] growth using coincidence, mutual sputtering,

or sputtering of Fe target in the case of heated Si substrate, it is adjusting the ratio of the inflow of the gas for sputtering, and hydrogen gas, and beta-FeSi 2 or amorphous FeSiX to which the hydrogen content was adjusted is produced. It is made for one component of neon, an argon, a krypton, and a xenon to be included in the rare gas for sputtering.

[0014]

By adjusting the pressure of the hydrogen gas in the ambient atmosphere at the time of thin film growth, the optical band gap of an iron silicide semi-conductor thin film is changeable by controlling the amount of hydrogen contained inside the thin film of beta-FeSi 2 or amorphous FeSiX. Furthermore, the film of a different optical band gap in the membranous depth direction is easily producible by changing hydrogen inflow and carrying out film production. While the degree of hydrogenation becomes large, an optical band gap increases.

[0015]

The electrical property of an iron silicide semi-conductor thin film is controllable by the effectiveness of reducing carrier concentration or making carrier concentration increasing by similarly controlling the amount of hydrogen contained inside beta-FeSi 2 or an amorphous FeSiX thin film.

Although the hydrogen content of the boundary to which reduce carrier concentration or carrier concentration is made to increase is about 10at%, when good for how to be present in this boundary size depending on the crystallinity of the generation film when bad, it shifts to the smaller one.

[0016]

Light and electronic devices, such as a photoelectron component produced using existing Si and an existing GaAs system semi-conductor and same pn junction mold photo detector, can be manufactured using the hydrogenation iron silicide semi-conductor thin film of this invention. Although the film in which pn junction is still shown was not obtained in beta-FeSi 2 or amorphous FeSiX which is not hydrogenated, the pn junction film has been realized for the first time using the iron silicide film which this invention hydrogenated. What is necessary is just to produce the beta-FeSi film of p mold on an n mold Si substrate to produce the pn junction film with silicon.

[0017]

Experiment 1

The property of the manufacture approach of the hydrogenation iron silicide thin film by the laser ablation method and the obtained thin film is explained concretely below.

After exhausting the inside of a vacuum chamber to 2x10 to 7 or less Torrs with a turbo molecular pump, in the vacuum chamber which flowed hydrogen in the 0.1-10Pa pressure range, the ArF excimer laser (wavelength of 193nm, FWHM=20ns) was condensed at the FeSi2 amorphous-alloy (99.99%) target of the presentation ratio 1:2, it irradiated at 45 degrees of incident angles, and film deposition was performed on Si substrate which separates 50mm and counters. Between target-substrates, the high-speed pivotable wing mold rotation filter was installed, and drop let was captured. 4 J/cm2 and a repetition frequency made 10Hz and substrate temperature a room temperature (20 degrees C) and 700 degrees C for the fluence F of a laser pulse.

[0018]

Evaluation of the generation film performed SEM observation, an X diffraction, light absorption spectrum measurement, and electric resistance measurement. It is amorphous FeSiX below 400 degrees C. It is amorphous FeSiX by changing the pressure of the hydrogen of a controlled atmosphere, although beta-FeSi 2 film generates above 400 degrees C. And beta-FeSi 2 was hydrogenated.

[0019]

Change (a is 2 theta-theta scan and b is 2theta scan) of the X diffraction pattern of beta-FeSi 2 film at the time of setting the pressure of hydrogen to 0Pa, 0.3Pa, and 3Pa at drawing 1 is shown. It turns out that the peak from beta-FeSi 2 is observed even if the pressure of hydrogen becomes high, and beta-FeSi 2 film is growing even if hydrogen mixes in a thin film. Amorphous FeSiX When it generates, since it is amorphous, a XRD peak is not observed irrespective of the pressure of hydrogen.

[0020]

To drawing 2 , it is hydrogenation amorphous FeSiX. A typical absorption spectrum is shown. The typical absorption spectrum of hydrogenation beta-FeSi 2 is shown in drawing 3 . Since fitting [ the band gap is increasing and / the square of an absorption coefficient ] compared with a hydrogen free-lancer's case both, it turns out that it is a direct transition mold.

[0021]
The dependency over the hydrogen pressure force (axis of abscissa : [Pa]) of an optical band gap (axis of ordinate: Eg [eV]) is shown in drawing 4 . An optical band gap increases with the increment in the hydrogen pressure force, i.e., the increment in the amount of hydrogen mixing in the film.
[0022]
The hydrogen pressure force (axis of abscissa : [Pa]) dependency of specific resistance (axis of ordinate: rhos [omega]) is shown in drawing 5 . For specific resistance, the direction of beta-FeSi 2 is amorphous FeSiX. Although it compares and is large a single figure, it decreases, once increasing with both increments in the hydrogen pressure force. When hydrogen mixes into the film shows that termination of the non-bonding electron is carried out, and carrier concentration decreases, and the non-bonding electron of hydrogen causing a carrier and reducing electric resistance, when hydrogen mixes too much.
[0023]
Experiment 2
The property of the manufacture approach of the hydrogenation iron silicide thin film by the opposite target type sputtering method and the obtained thin film is explained concretely below.
The inside of a chamber was exhausted to 10 - 4 or less Pa using the turbo molecular pump, Ar gas and hydrogen gas were flowed in the chamber, and total pressure was set to 1.33x10 to 1 Pa. In a target, it is FeSi2 of the presentation ratio 1:2. The alloy (99.99 %) was used. Applied voltage and a current are set to 950mV and 6.0mA, respectively, and it is amorphous FeSiX at a room temperature (20 degrees C) and 700 degrees C on Si substrate, respectively. And thickness about 240 nm membrane formation of beta-FeSi 2 was carried out.
[0024]
Evaluation of the generation film performed SEM observation, an X diffraction, light absorption spectrum measurement, and electric resistance measurement. below 400 degrees C, amorphous -like FeSiX performed hydrogenation of amorphous-like FeSiX and beta-FeSi 2 by adjusting the ratio of argon gas and hydrogen gas, although beta-FeSi 2 film generated above 400 degrees C.
[0025]
The X diffraction pattern of hydrogenation beta-FeSi 2 film obtained by drawing 6 is shown. Moreover, the X diffraction pattern of the hydrogenation amorphous FeSiX film obtained by drawing 7 is shown. As shown in drawing 6 , irrespective of a hydrogen partial pressure, the diffraction peak of beta-FeSi 2 is observed and hydrogenated beta-FeSi 2 is growing. As shown in drawing 7 , at the room temperature, irrespective of a hydrogen partial pressure, a broadcloth peak is observed and amorphous FeSiX is growing.
[0026]
The typical absorption spectrum of amorphous FeSiX which is not hydrogenated by drawing 8 is shown. Moreover, FeSiX hydrogenated by drawing 9 A typical absorption spectrum is shown. Since an absorption spectrum is in a straight line mostly when an axis of ordinate is the square of an absorption coefficient, it turns out that it is a direct gap semiconductor. It turns out that the band gap is [ the direction of the hydrogenated thin film ] large.
[0027]
The typical absorption spectrum of non-hydrogen beta-FeSi 2 is shown in drawing 10 . Moreover, the typical absorption spectrum of hydrogenation beta-FeSi 2 is shown in drawing 11 . Like amorphous FeSiX, it is a direct gap semiconductor and the band gap is [ the direction of hydrogenation beta-FeSi 2 ] large.
[0028]
The change to the hydrogen partial pressure (PH2/PAr) of an optical band gap (axis of ordinate: Eg [eV]) is shown in drawing 12 . It turns out that the optical band gap is increasing while a hydrogen partial pressure becomes high, and an optical band gap becomes large while the hydrogen content in a thin film becomes large.
[0029]
The change to the hydrogen partial pressure (PH2/PAr) of specific resistance (axis of ordinate: rhos [omega]) is shown in drawing 13 . Once specific resistance increases with the increment in the pressure of hydrogen, it decreases. When hydrogen mixes into a thin film shows that termination of the non-bonding electron is carried out, and carrier concentration decreases, and the non-bonding electron of hydrogen causing a carrier and reducing electric resistance, when hydrogen mixes too much.
[0030]

[Example]
Example 1
The photoelectron component produced using existing Si and an existing GaAs system semi-conductor and the same component were produced using hydrogenation beta-FeSi 2 which formed membranes depending on the method of opposite target type DC sputtering. FeSi2 of the presentation ratio 1:2 which made the target dope P (Lynn) 1019cm-1 FeSi2 of the presentation ratio 1:2 which made an alloy (99.99 %) and B (boron) dope 1015cm-1 The alloy (99.99 %) was used. After exhausting the inside of a chamber below to 10-4 Pa using a turbo molecular pump, it added the hydrogen gas of 15sccm(s) to Ar gas, flowed into it, and formed membranes by setting total pressure in a chamber to 1.33x10-1 Pa.
[0031]
Substrate temperature was made into 600 degrees C at the substrate using insulating quartz glass. 30 nm laminating of n mold hydrogenation beta-FeSi 2 was carried out using the target with which B was doped 5 micrometers and after that in p mold hydrogenation beta-FeSi 2 using the target with which P was doped first on the substrate.
[0032]
Hydrogenation beta-FeSi 2 is used for drawing 14 , p mold hydrogenation beta-FeSi 2 thin film 2 is formed on the insulating quartz-glass substrate 1, n mold hydrogenation beta-FeSi 2 thin film 3 is further formed on it, and the structure of the pn junction mold photo detector which formed the electrode 4 at each of p mold hydrogenation beta-FeSi 2 thin film 2 and n mold hydrogenation beta-FeSi 2 thin film 3 is shown typically.
[0033]
The I-V property of this component is shown in drawing 15 . The I-V property typical to pn junction was observed by the case where light is not irradiated, and the case where it irradiates, like the p-n junction component using Si. The intercept of V shaft at the time of an optical exposure and an I-axis is called open circuit voltage and a short-circuit current, respectively, and it is equivalent to the maximum electric power which can be taken out when these products think as an optoelectric transducer. Clear open circuit voltage and a short-circuit current existed, it turned out that it is functioning as a photoelectric element, and it was checked that pn joint film was realizable by beta-FeSi 2.
[0034]
[Effect of the Invention]
The iron silicide semi-conductor thin film of this invention can also realize an optoelectric transducer with different photosensitivity on the same component while enabling control of light and an electrical property by giving a desired band gap, when using to various devices.
[Brief Description of the Drawings]
[Drawing 1] It is the X diffraction pattern of hydrogenation beta-FeSi 2 film produced in the experiment 1.
[Drawing 2] It is the typical absorption spectrum of the hydrogenation amorphous film (0.3Pa of hydrogen pressure force) produced in the experiment 1.
[Drawing 3] It is the typical absorption spectrum of hydrogenation beta-FeSi 2 film (hydrogen pressure force 0.3 Pa) produced in the experiment 1.
[Drawing 4] It is the graph which shows change of the optical band gap to the hydrogenation amorphous film produced in the experiment 1, and the hydrogen pressure force of beta-FeSi 2.
[Drawing 5] It is the graph which shows change of the specific resistance to the hydrogenation amorphous film produced in the experiment 1, and the hydrogen pressure force of beta-FeSi 2.
[Drawing 6] It is the X diffraction pattern of hydrogenation beta-FeSi 2 film produced in the experiment 2.
[Drawing 7] It is the X diffraction pattern of the hydrogenation amorphous FeSiX film produced in the experiment 2.
[Drawing 8] It is the typical absorption spectrum of the amorphous FeSiX film which was produced in the experiment 2 and which is not hydrogenated.
[Drawing 9] It is the typical absorption spectrum of the hydrogenation amorphous FeSiX film produced in the experiment 2.
[Drawing 10] It is the absorption spectrum of beta-FeSi 2 film which was produced in the experiment 2 and which is not hydrogenated.
[Drawing 11] It is the typical absorption spectrum of hydrogenation beta-FeSi 2 film produced in the

experiment 2.
[Drawing 12] It is the graph which shows change of the optical band gap accompanying hydrogenation of hydrogenation amorphous FeSi2 (700 degrees C) produced in the experiment 2, and beta-FeSi 2 (30 degrees C).

[Drawing 13] It is the graph which shows change of the specific resistance accompanying hydrogenation of hydrogenation beta-FeSi 2 (700 degrees C) produced in the experiment 2, and amorphous FeSi2 (30 degrees C).

[Drawing 14] It is the mimetic diagram of the structure of the pn junction mold photo detector using hydrogenation beta-FeSi 2 produced in the example 1.
[Drawing 15] It is the graph which shows the I-V property of the pn junction mold photo detector using hydrogenation beta-FeSi 2 produced in the example 1.

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DRAWINGS

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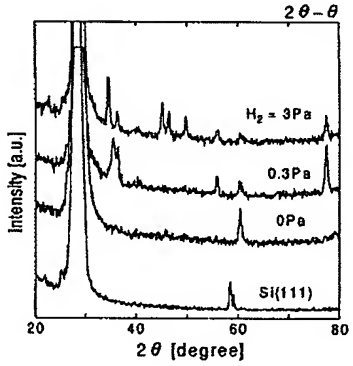
[Drawing 1]

(a)

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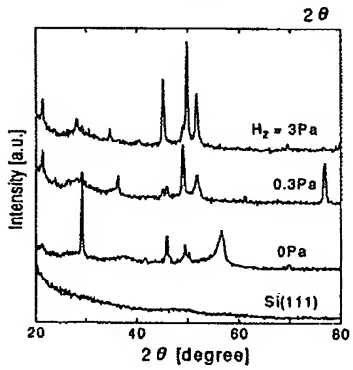
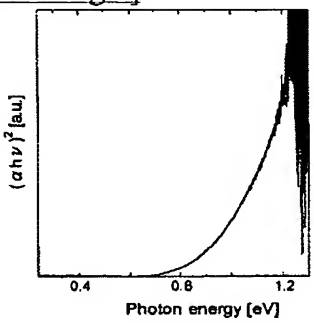
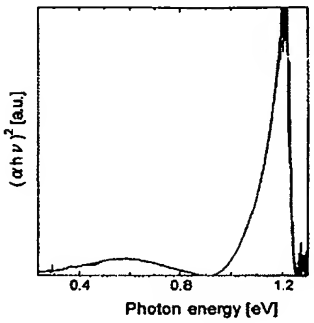


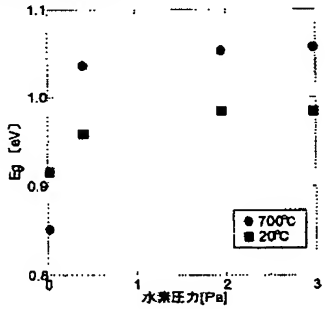

[Drawing 2]



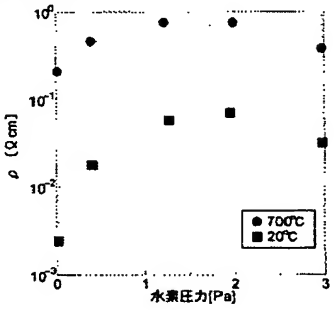

[Drawing 3]



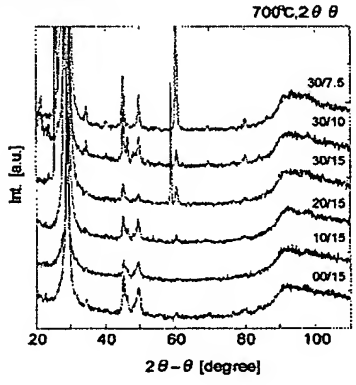

[Drawing 4]



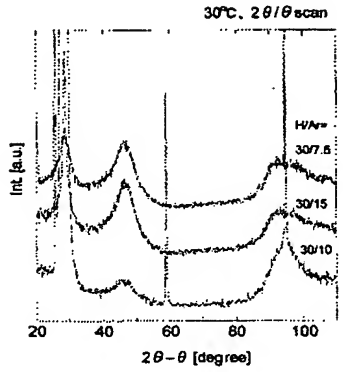

[Drawing 5]



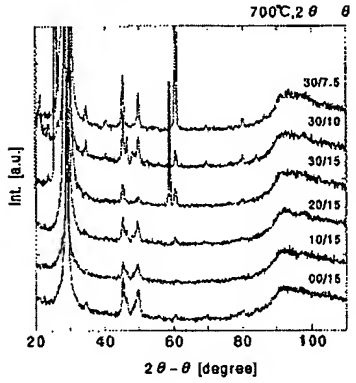

[Drawing 6]



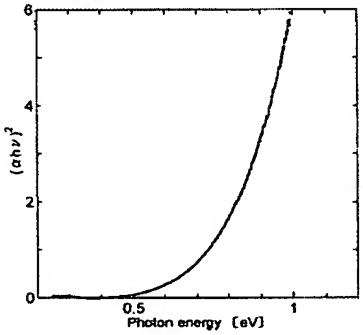

[Drawing 7]



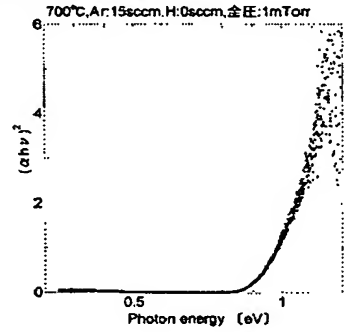

[Drawing 8]



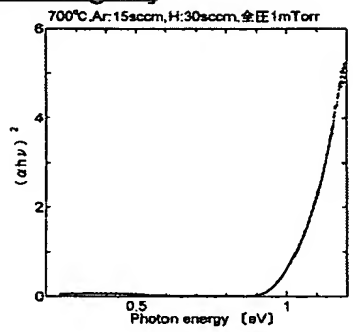

[Drawing 9]



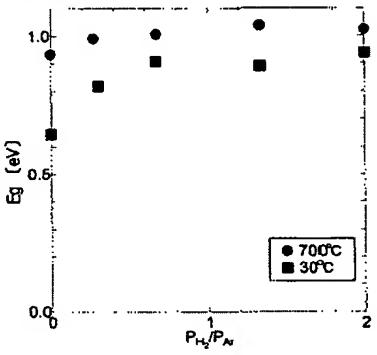

[Drawing 10]



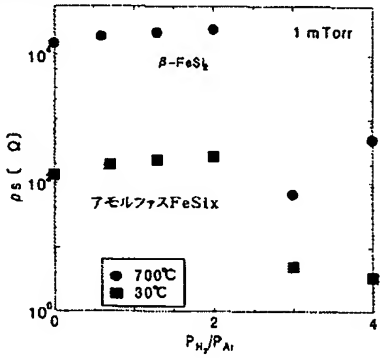
[Drawing 11]



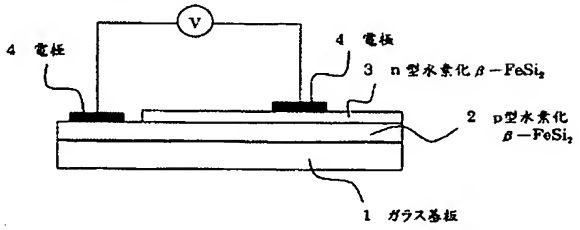

[Drawing 12]



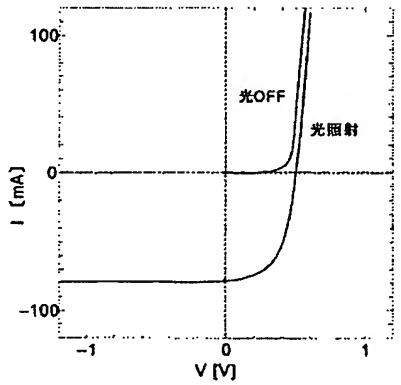

[Drawing 13]




[Drawing 14]



[Drawing 15]

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